



DEVELOPMENT OF THE *FR 13* RISK FRAMEWORK
– DEMONSTRATED WITH ONE- AND TWO-STEP
STEADY-STATE MEMBRANE PROCESSING
OF JUICES

by

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STATEMENT OF DECLARATION

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¹ Davey, K.R., Zou, W., 2015. Fruit juice processing and membrane technology application (*sic*) – A response. *Food Eng. Rev.* – submitted Oct. 2015.

Zou, W., Davey, K.R., 2014. A *Friday 13th* risk model for failure in cross - flow membrane filtration of passion fruit juice. In: Proc. 26th European Modelling and Simulation Symposium - EMSS 2014, Sept. 10 – 12, Bordeaux, France, paper 106. [ISBN: 9788897999386](#)

Zou, W., Davey, K.R., 2014. A novel *Friday 13th* stochastic assessment of failure of membrane filtration in juice clarification. In: Proc. 44th Australasian Chemical Engineering Conference (Processing Excellence, Powering our Future). Sept. 27 – Oct. 1, Perth, WA, Australia, paper 1259. [ISBN/ISSN: 1922107387](#)

Zou, W., Davey, K.R., 2015. An integrated two-step *Fr 13* synthesis – demonstrated with membrane fouling in combined ultrafiltration-osmotic distillation (UF-OD) for concentrated juice. *Chem. Eng. Sci.* – submitted on Nov. 2015.

EXECUTIVE SUMMARY

Steady-state processing is used extensively in foods and chemical, engineering, and more widely. Importantly, however there will be naturally occurring, random fluctuations in parameter values about an apparent steady-state 'set' mean. These are not sufficient, on their own, to be considered transient i.e. unsteady-state. Generally, random small change in one parameter is 'off-set' by a corresponding change in another - with the output seemingly remaining steady. Traditional chemical engineering does not address these random fluctuations explicitly.

However, Davey and co-workers (e.g. [Abdul-Halim and Davey, 2015 a, b](#); [Davey, 2015 a](#); [Davey et al., 2016](#)) have reasoned that process failures can result from the accumulation of these fluctuations within an apparent steady-state process itself. Their hypothesis is that naturally occurring chance fluctuations can unexpectedly combine and accumulate in one direction and leverage significant change across a binary 'not failure - failure' boundary. That is to say, even with good design and operation of plant, there can be unexpected (surprise and sudden) occasional failures. This they titled *Fr 13 (Friday 13th)* to underscore the nature of the event. A current limitation of the *Fr 13* framework however that is it has been largely limited to one-step (single) unit-operations. It was not known therefore if there was any benefit in developing the framework as a useful tool for integrated multi-step foods and chemicals engineering unit-operations.

A research program was therefore undertaken with the aim to advance the *Fr 13* framework to gain unique insight into how naturally occurring fluctuations in apparent steady-state plant parameters can be transmitted and impact in progressively complex (in the context of 'integrated' not 'complicated') multi-step processes, and to assess the *Fr 13* framework as a new design tool.

A logical and stepwise approach was implemented as a research strategy.

Because steady-state membrane clarification and concentration of fruit juices is becoming a widespread alternative to traditional thermal treatments, a two-step membrane concentration was selected as a timely and stringent test of development of the *Fr 13* risk thesis.

Two, preliminary single-step *Fr 13* membrane models, ‘dead-end’ and ‘cross-flow’, were initially synthesized and tested with independent experimental data for clarification of orange ($n = 25$) and blood orange ($n = 34$) juice. *Fr 13* simulations of the key input parameters, transmembrane pressure (ΔP), filtration time (t) and volumetric flow rate (Q), revealed that some 16.8 % of dead-end and 4.0 % of cross-flow membrane filtrations, over an extended time, will fail to meet the required operational flux plus a practical tolerance (2 %) as a design margin of safety. If each filtration is thought of as a daily batch-continuous operation, then an unexpected fouling failure could result every six (6) and 26 days, respectively, in batch-continuous processing.

A more commercially representative integrated two-step *Fr 13* membrane global model was then synthesized for combined ultrafiltration (UF) - osmotic distillation (OD) (UF-OD), and validated with extensive independent data ($n = 27$) for pomegranate (*Punica granatum*) juice. Overall global failure of the integrated two-step UF-OD was defined as a fouled (unwanted) OD flux. *Fr 13* simulations showed that the integrated UF-OD is expected to be vulnerable to surprise fouling failure in 10.5 % of all operations over an extended time. This translates to 39 surprise failures per year with a 3 % design tolerance. In completing this work an important error in the membrane literature was discovered, corrected and addressed².

Fr 13 simulations of these newly synthesized models underscored that the three (3) apparent steady-state membrane processes should be more correctly thought of as a combination of successful and failed operations. This new insight is not available from traditional risk and hazard analyses, with or without sensitivity analyses.

Findings were applied in ‘second-tier’ studies to assess re-design of membranes processing of juices. The aim was to improve process reliability and reduce vulnerability to unexpected failure. For example, repeat *Fr 13* simulations revealed that for the integrated

² The permeate flux (J_0) used for measuring membrane permeability was found to be widely incorrectly defined e.g. by [Schafer et al. \(2005\)](#), [Boerlage et al. \(2002\)](#) and [Echavarría et al. \(2011\)](#) in which it was not possible to reconcile the form or units in engineering science. The effect was to significantly overestimate the predicted vulnerabilities to *Fr 13* fouling failure, in the preliminary work. This is being addressed by [Davey and Zou \(2015\)](#) (*see Appendix C*).

UF-OD, reducing variance about the mean value of transmembrane pressure ($\Delta P_{UF\ 1-1}$) and filtration time ($t_{UF\ 1-1}$) of UF significantly reduces overall UF-OD failures (p_2). Practically, this suggests costs for increased precision control to limit fluctuations in the UF parameters could be readily justified.

Further, second-tier simulations of the integrated UF-OD showed that the addition of an enzymatic treatment step prior to UF could significantly reduce the overall UF-OD failures through a reduction in the required (design) operational UF flux ($J_{UF\ 1-1, required}$).

These findings will aid an enhanced understanding of factors that contribute to unwanted fouling as membrane failure, and to increased confidence in steady-state membranes operations.

It is concluded that the *Fr 13* framework is generalizable to an integrated two-step, steady-state processes. Additionally, there appears no methodological barriers to advancement. Therefore results auger well for further advancement of the *Fr 13* framework to a range of steady-state processes of increasing complexity and inter-connectedness. If properly developed, it is thought that *Fr 13* could become a new decision tool, in both design analysis and synthesis, for improved understanding of process behaviour outcomes.

This research is original and not incremental work. Outcomes are of immediate interest to researchers in risk analyses and processors and manufacturers of membrane equipment.

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